On-line and in situ gas (tar) measurements

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Outline

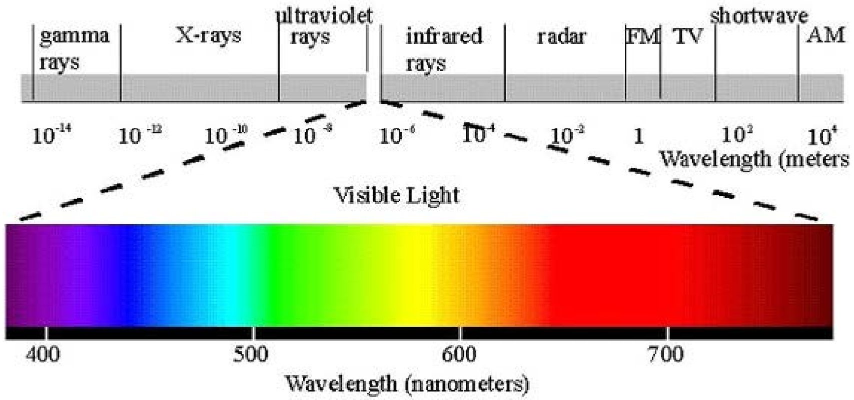
- **Introduction to Optical Absorption Spectroscopy / DOAS**
  - Choice of spectral range
  - Choice of medium

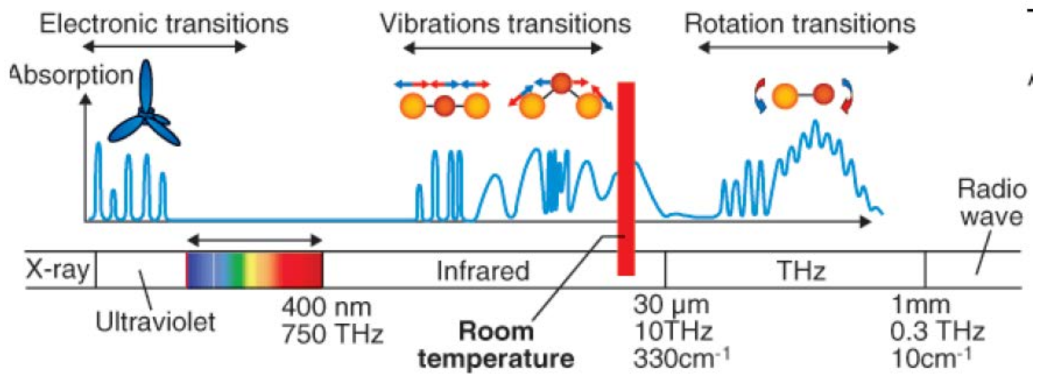
- **Before real measurements:**
  - Gas cell and setup
  - Temperature-dependent Absorption Cross-Sections Database

- **Real measurements:**
  - What can we expect?
  - Viking (high-T gasification)
  - LT-CFB (low-T gasification)
  - “Bad” grade wood fired burner (uncomplete combustion)

- **Conclusions**

Choice of spectral range





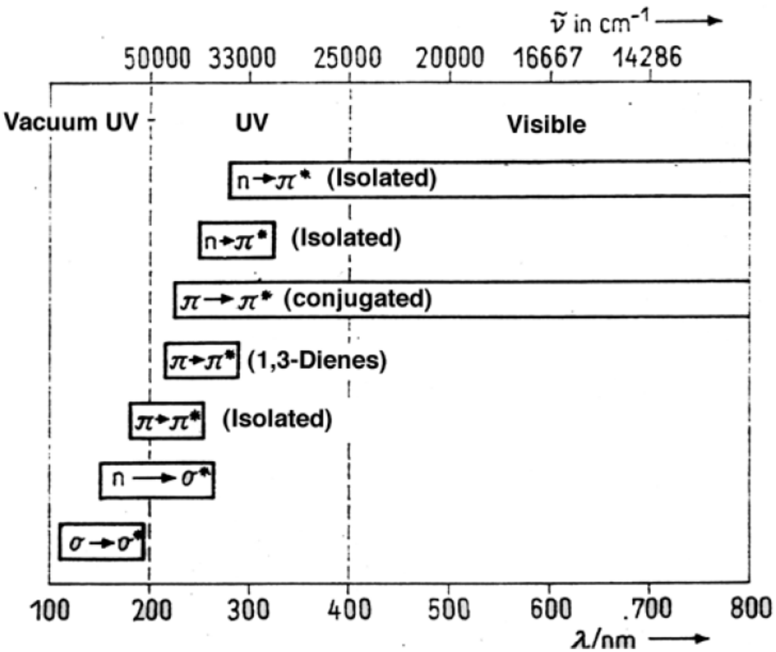
UV (200nm<λ):

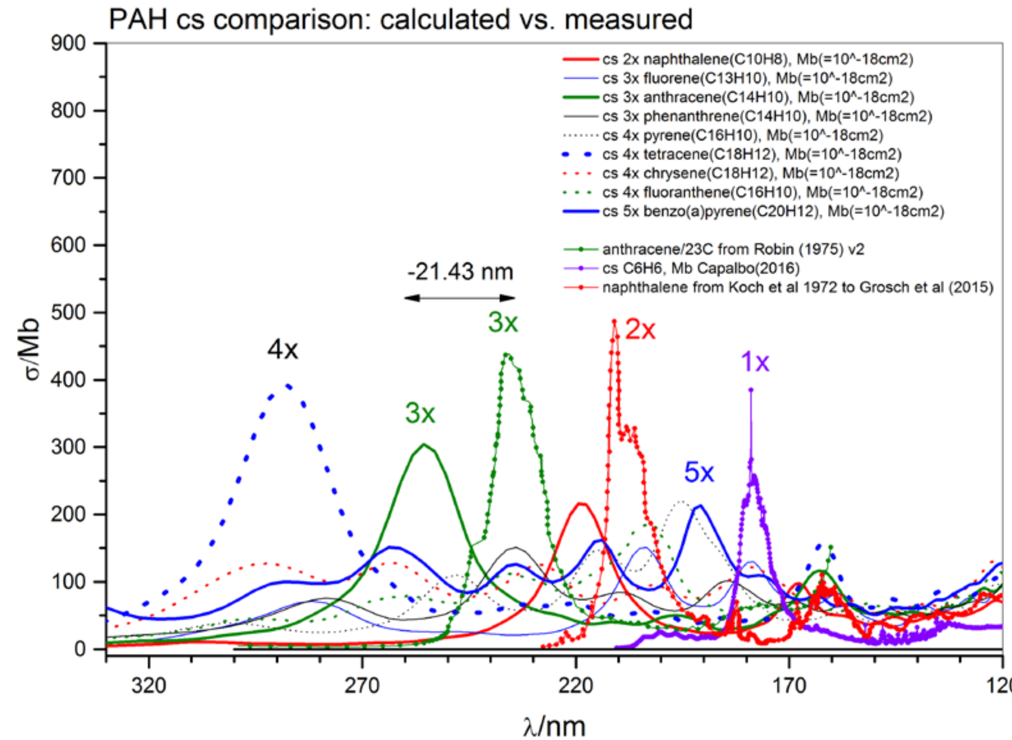
- superb sensitivity for organics;
- (very) strong light absorption;
- in situ or on-line measurements.

Special for gasification: no O_2

- possibility to go further down (120nm<λ): **far UV**;
- superb sensitivity for major/minor gas components;
- compact system;
- in situ or on-line measurements.

Choice of spectral range



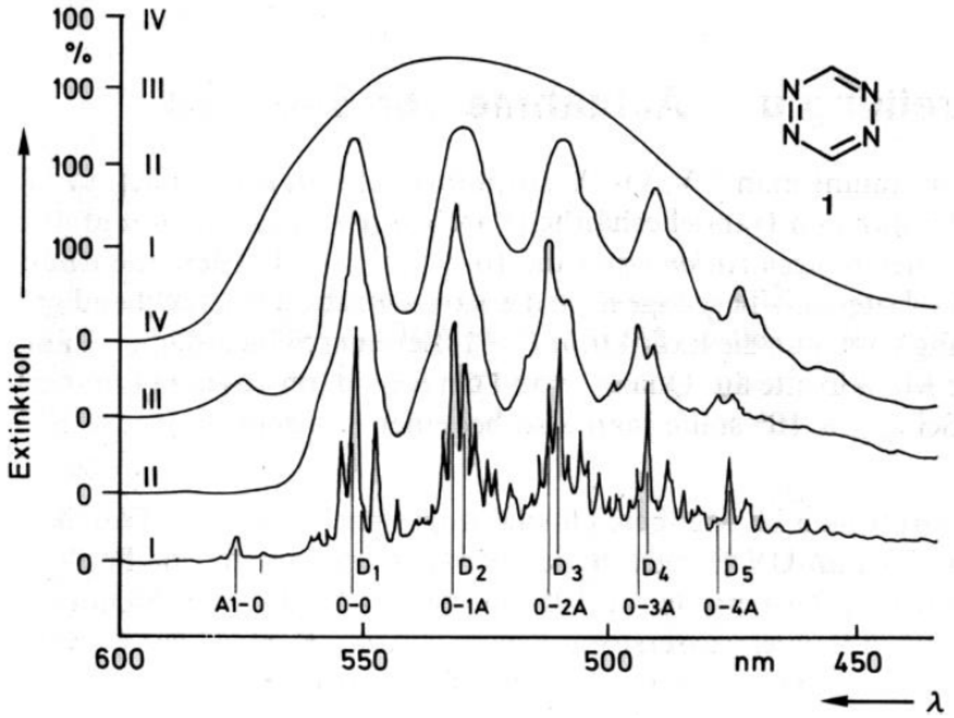


- **Larger cross-sections (cs) → stronger absorption → easy to measure**
- More (benzene) rings (+substitutes) → absorption at longer λ
  - Tar has strong UV absorption at **200nm<λ**
  - *cs for 1x to 5x about the same magnitude(5x = number of benzene rings)*
- BTX and light PAH's have strong UV absorption in **170-200nm**
- **120-170nm** is tar-"free" region: major/trace gas analysis (H_2O, CO_2, CO, saturated unsaturated (double/triple C-C and C=O) hydrocarbons)

1Mb=1x10^{-18} cm^2

Choice of medium

Example: 1,2,4,5-tetrazine



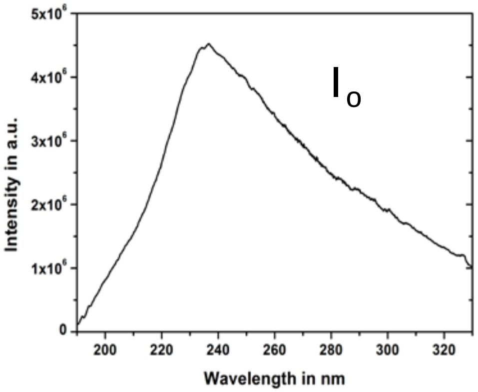
I	Gas phase, room temperature
II	In isopentane-methylcyclohexane matrix, 77K
III	In cyclohexane, room temperature
IV	In water, room temperature

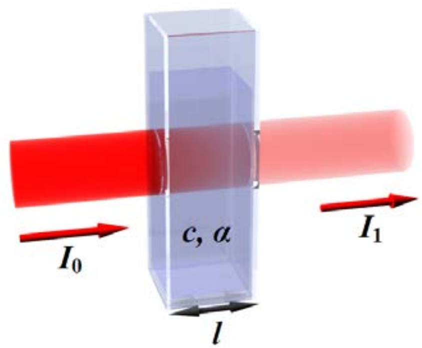
- Molecules have their own “fingerprints”
- Vibrational fine structure disappears in solutions but not in the gas phase
- Fine structure degrades with temperature

Introduction to Optical Absorption Spectroscopy / DOAS

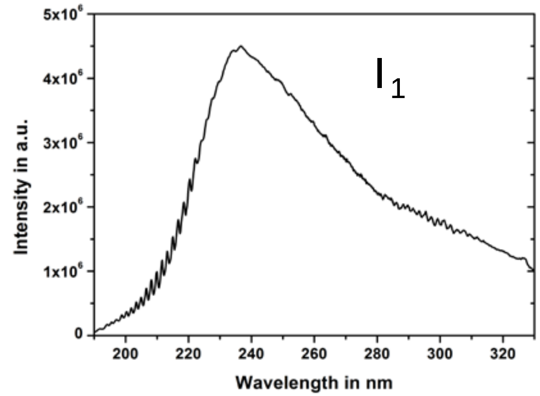
Lambert Beer Law

Spectrum w/o absorption





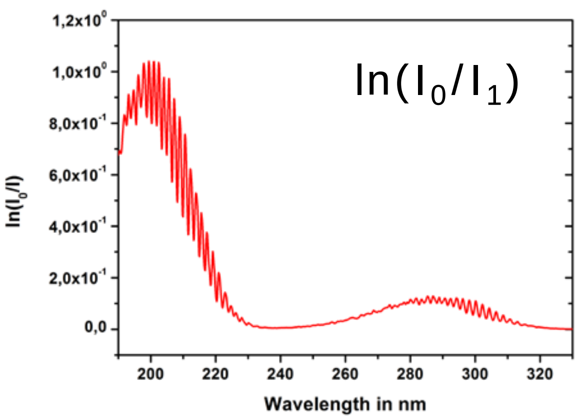
Spectrum with absorption

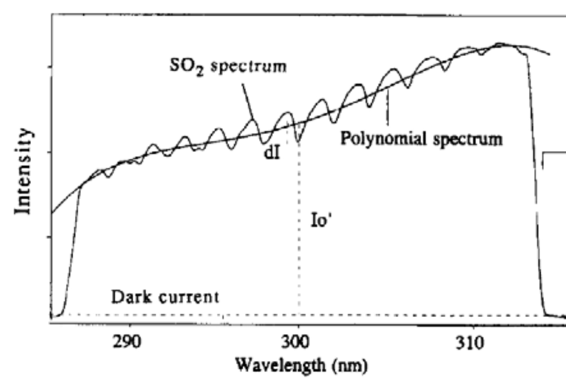


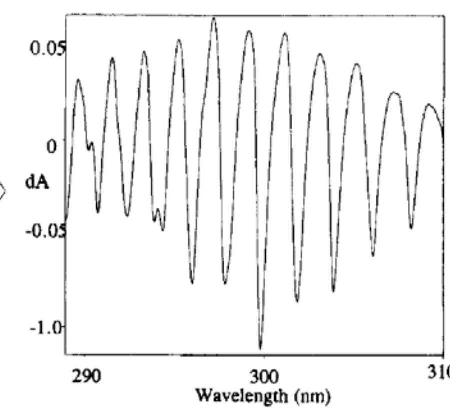
$$\frac{I_1}{I_0} = e^{-\alpha \cdot l} = e^{-\sigma \cdot N \cdot l}$$

$$\ln \frac{I_0}{I_1} = \sigma \cdot N \cdot l$$

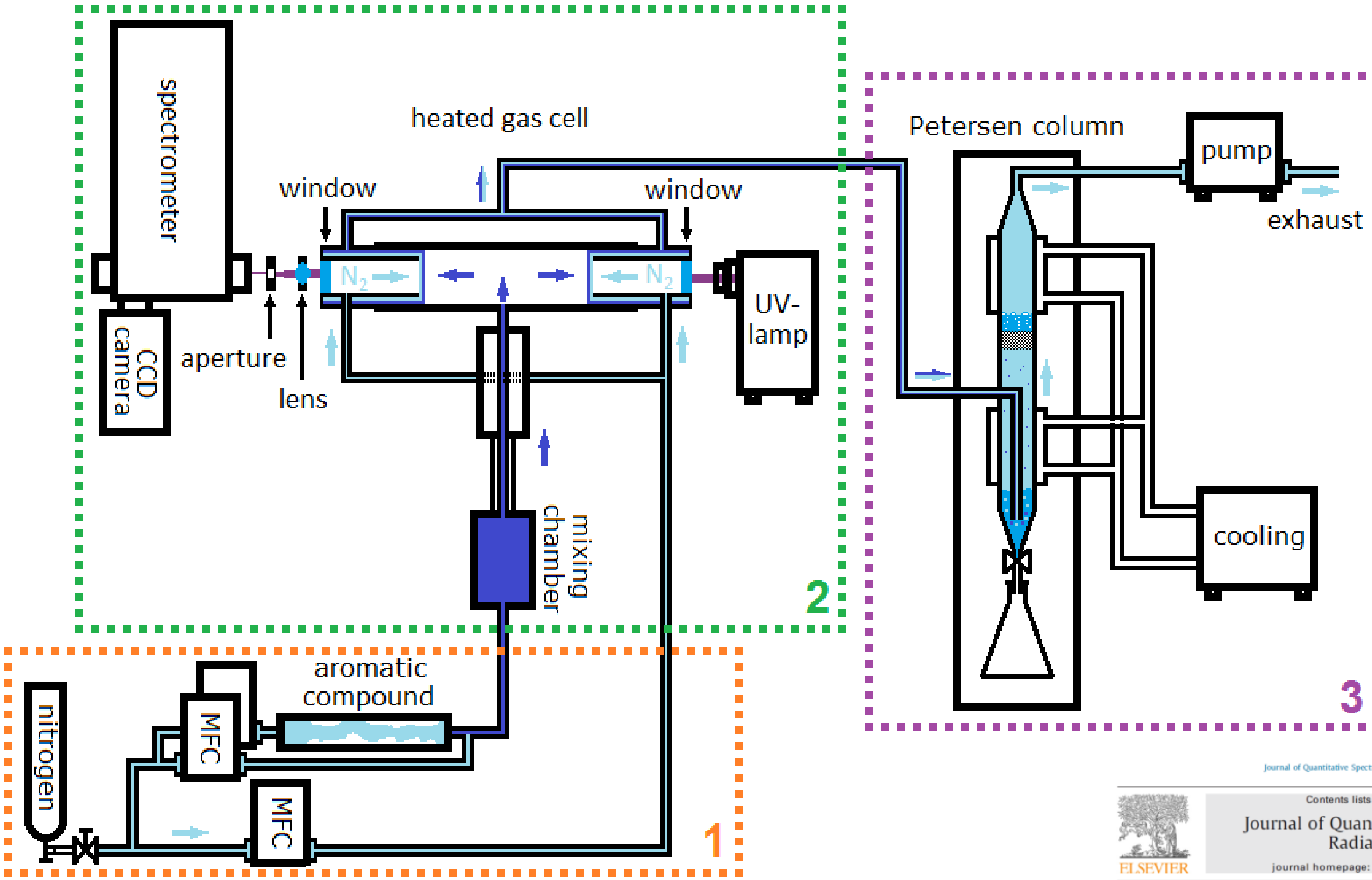
σ: absorption cross-section (CS)
N: gas density

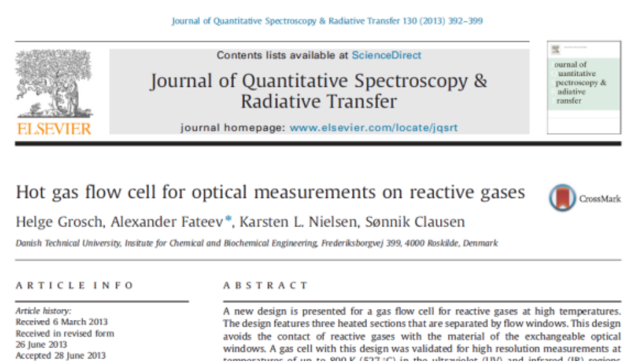






Set Up for UV Absorption Cross-Sections Measurements with Reactive Gases





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Hot gas flow cell for optical measurements on reactive gases

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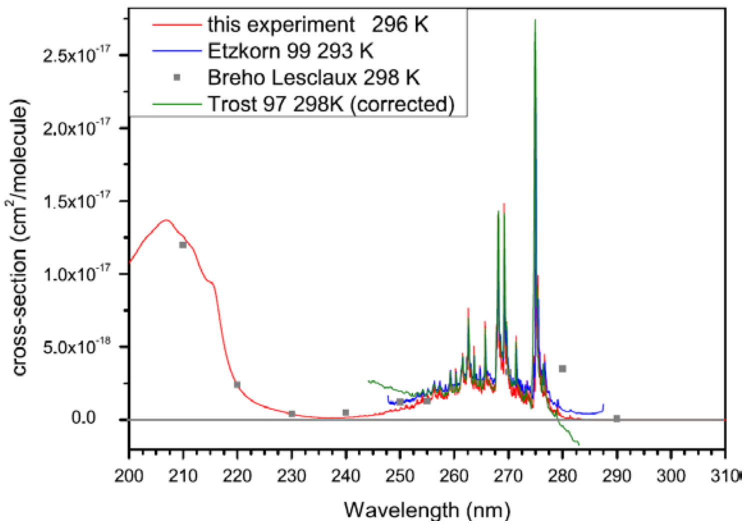
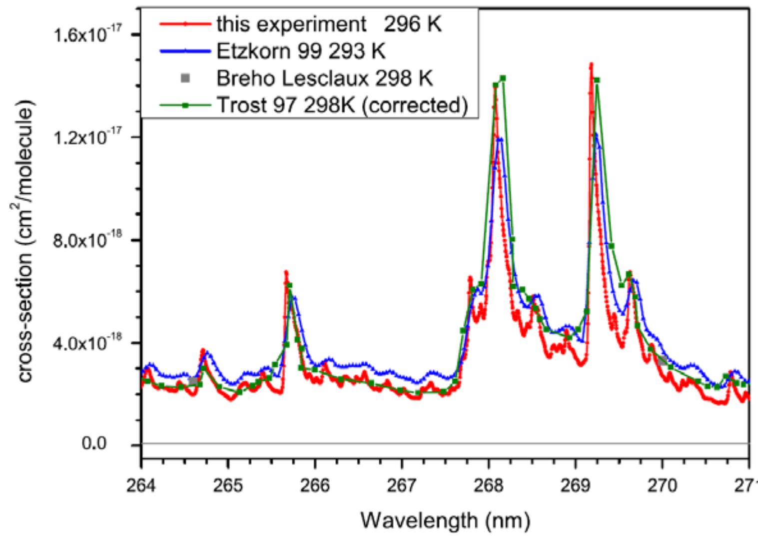
ABSTRACT

A new design is presented for a gas flow cell for reactive gases at high temperatures. The design features three heated sections that are separated by flow windows. This design avoids the contact of reactive gases with the material of the exchangeable optical windows. A gas cell with this design was validated for high resolution measurements at

Set Up’s validation: Absorption Cross-Sections at 22C

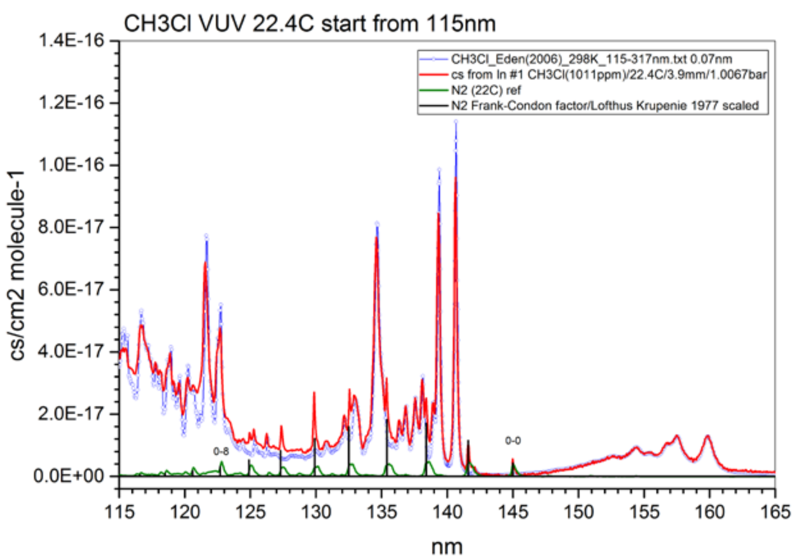
Phenol

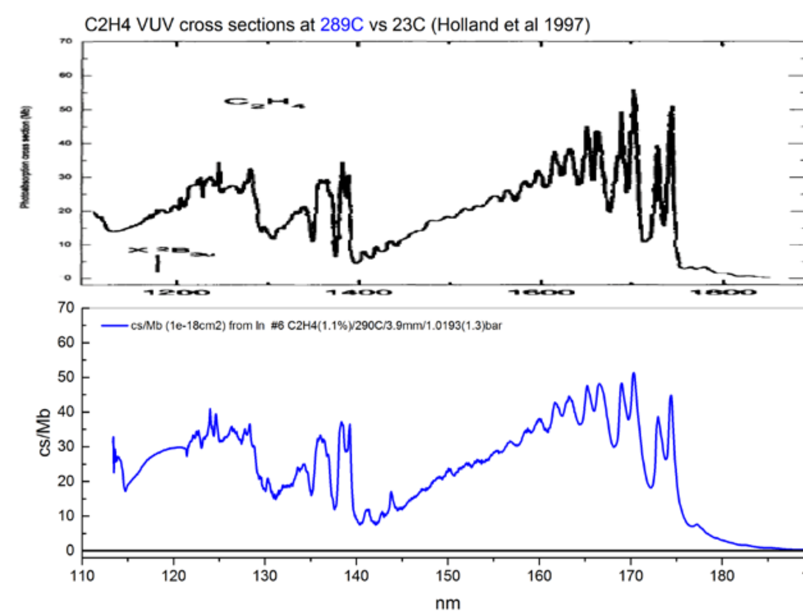




MeCl

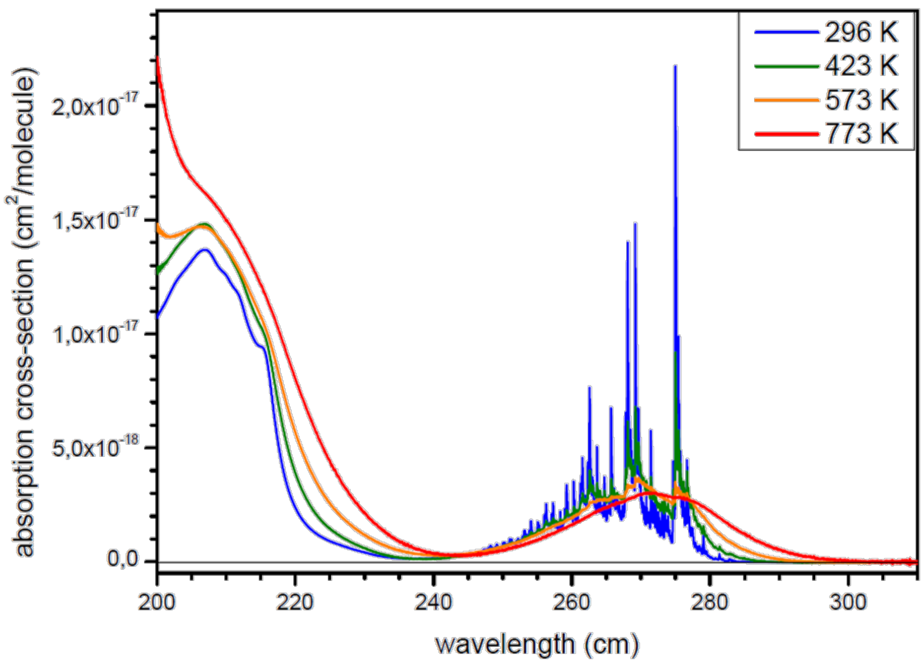
Ethylene (23C vs 289C)



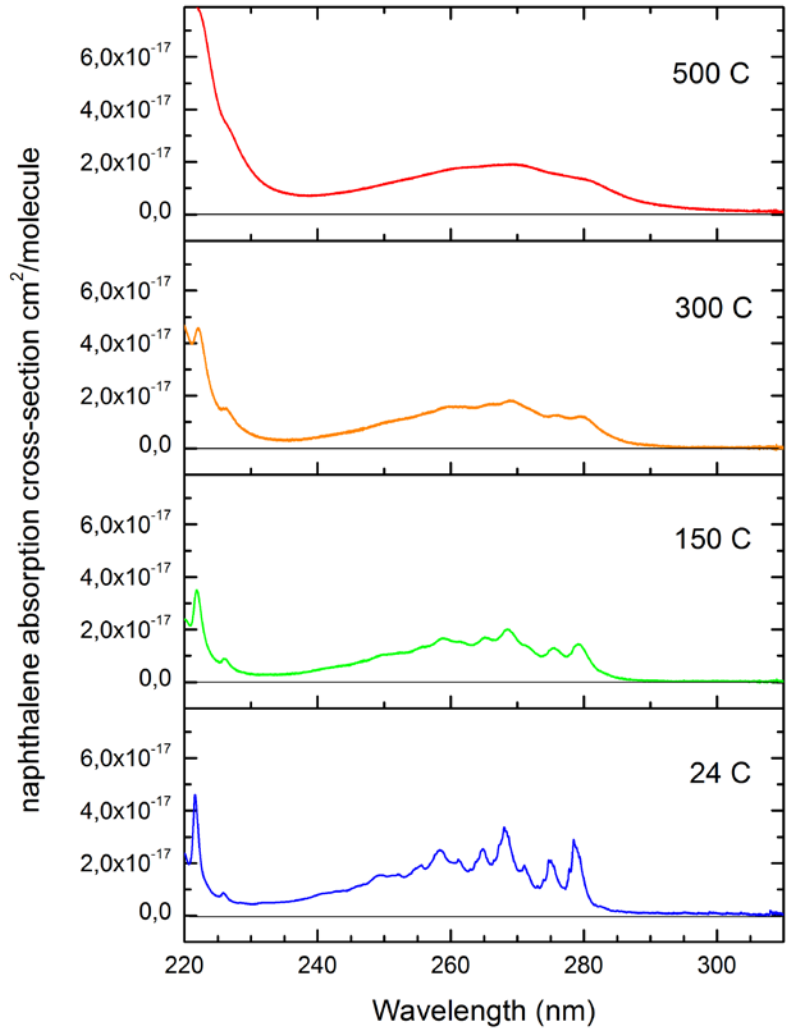


T-dependent Absorption Cross-Sections

Phenol



Naphthalene

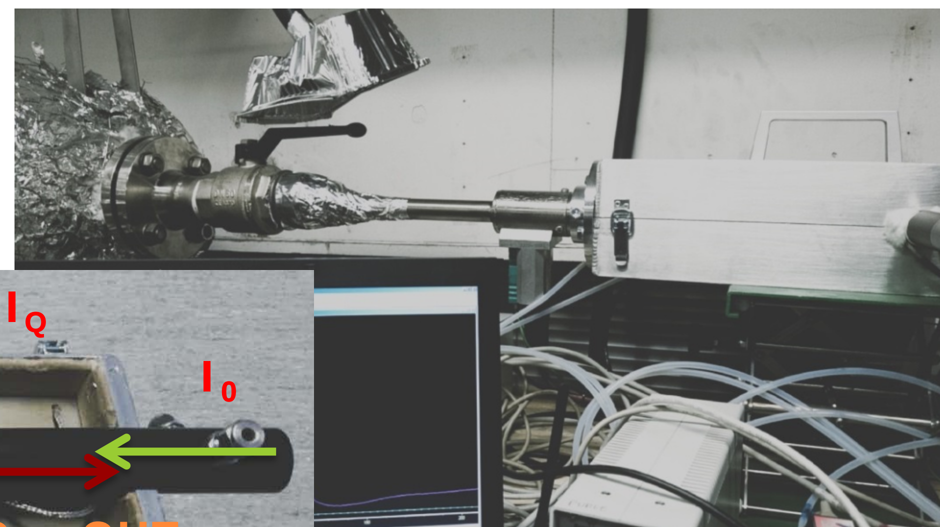


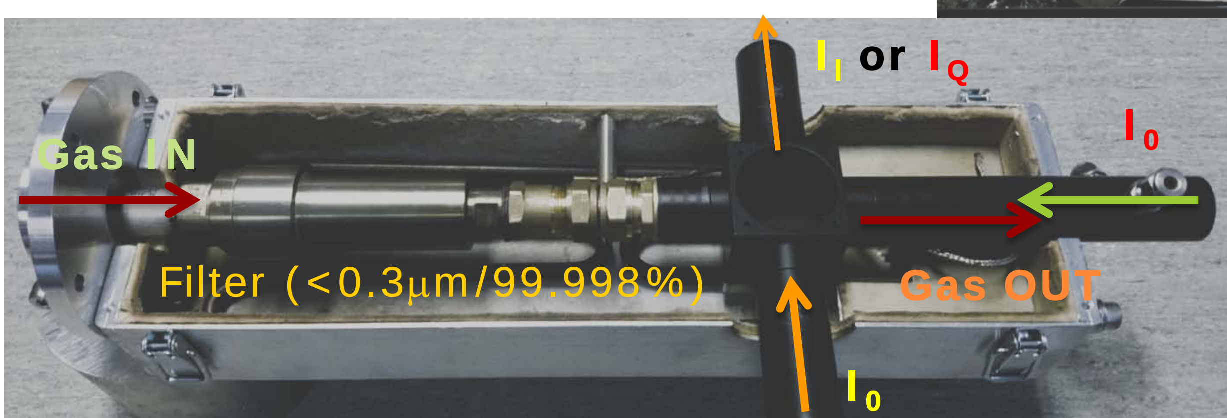
With T-raise:

- “coarse” structure widens
- “fine” structure” disappears

→ Keep T as low as possible

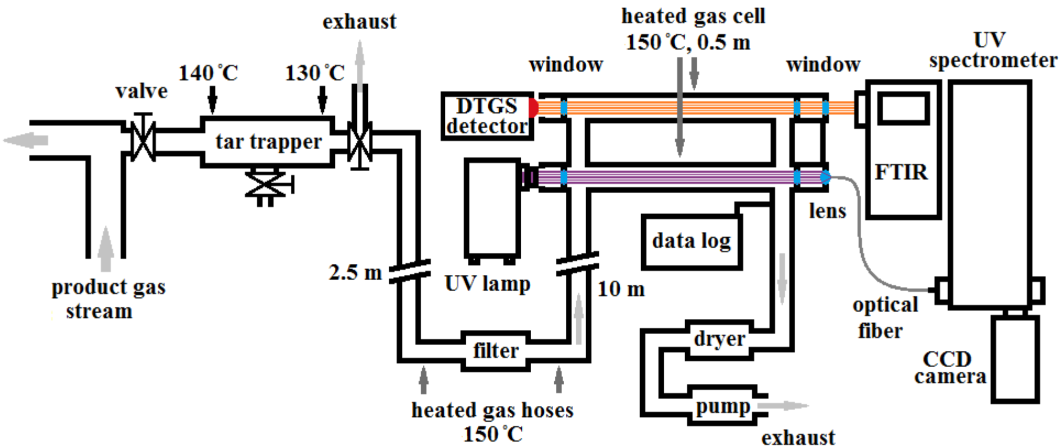
Set Ups for real measurements: how do they look?





Setup: on-line gas extraction vs in situ

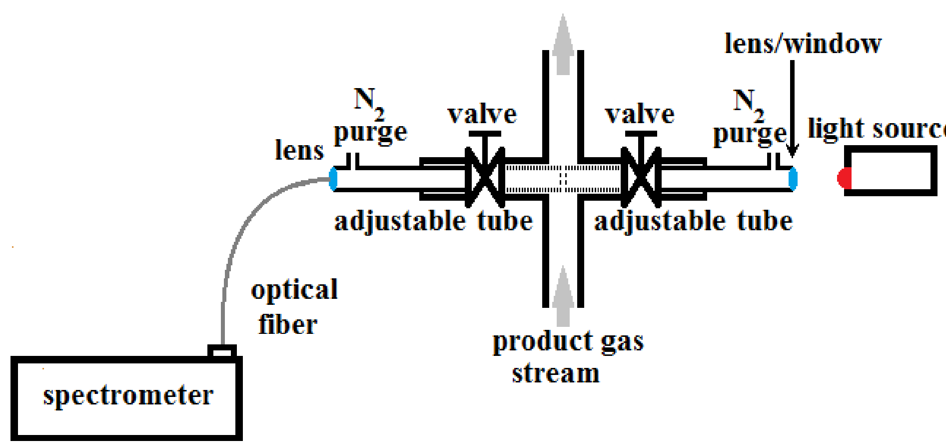
Extraction



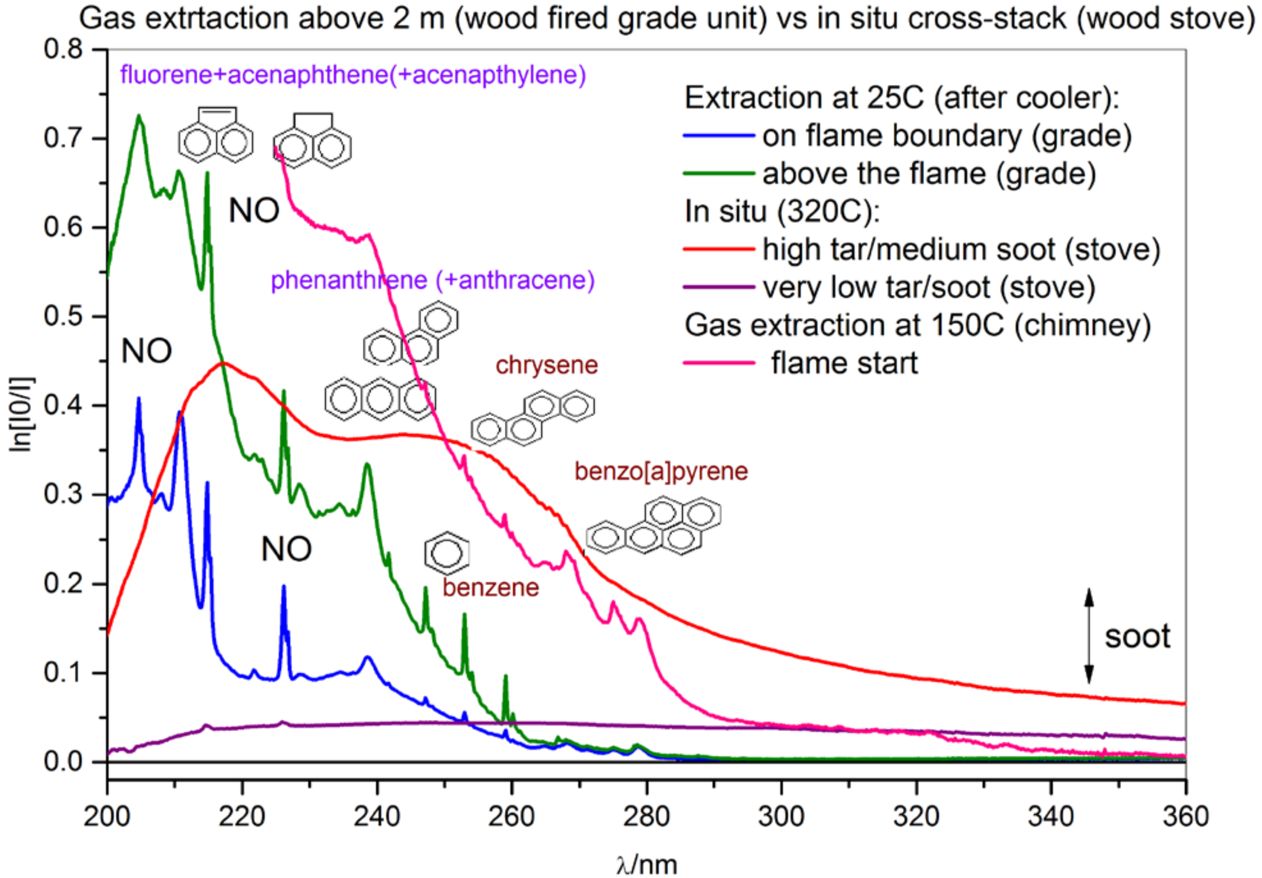
- extraction from 300 C
- tar trapper (at 130 C)
- Fully heated system (150 C)
- particle filter
- 2x 0.5 m gas cell (IR + UV parallel)
- same optical equipment as in lab

In-situ

- in-situ measurements
- optical windows purged with N_2
- same optical equipment as in lab
- use of optical fibers

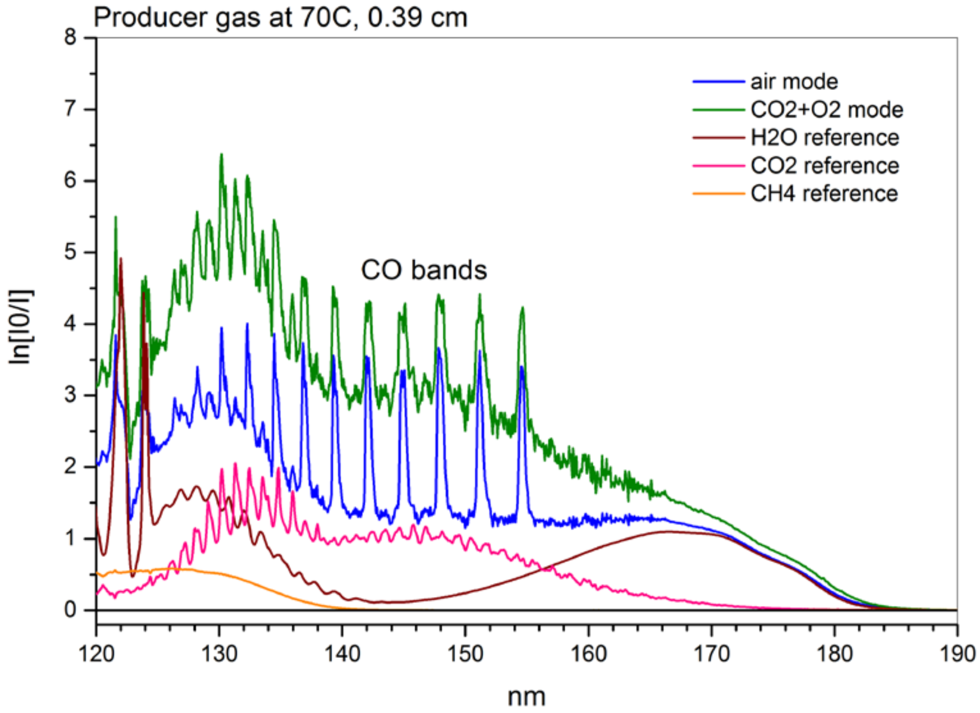


What can we expect?



- After gas cooler (**5C**): no water but still some tar/PAH's: easy to identify
- Measurements after filter at **150C**: condensable (= water soluble) vs rest
- NO clear signature
- **Tar / soot / NO / … can be measured with time resolution**

Clean (from tar) gas: Viking gasifier



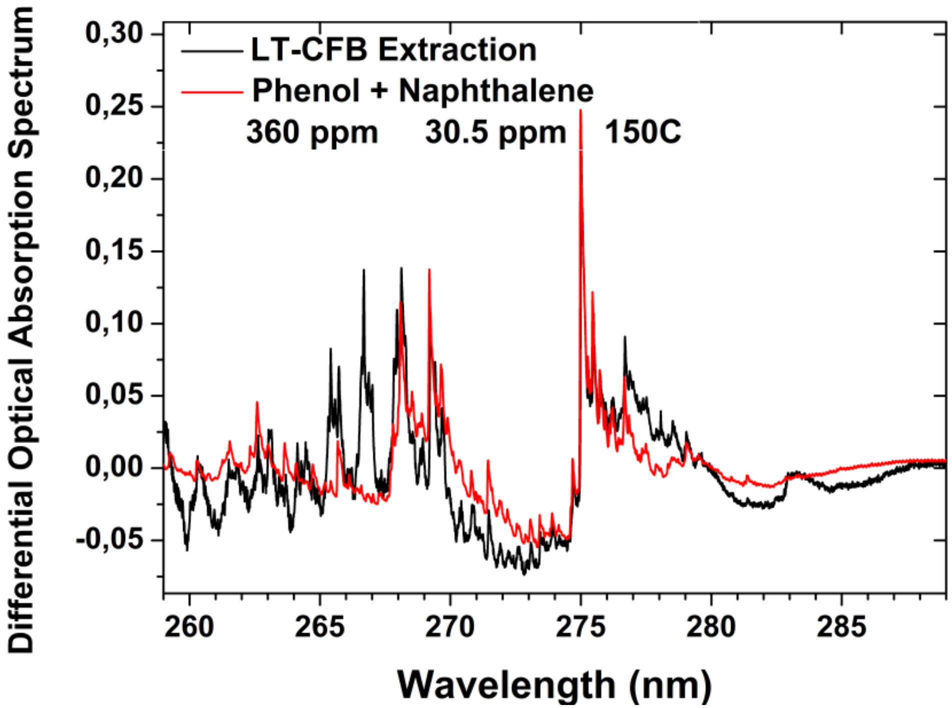
Viking	Air ***	O_2-CO_2 1st run ***	O_2-CO_2 2nd run***
CH_4	0.433%	0.866%	1.028%
CO_2	12.2%	31.08%	24.42%
H_2O	2.74%	2.82%	2.8%
O_2	0.354%	0.885%	0.955%
CO	8%	14%	14%
N_2	77%	0%**	0%**
NH_3	33ppm	0ppm**	0ppm**
C_6H_6	0ppm**	22ppm	22ppm
CH_3CHO*	0pmm**	100ppm	100ppm
OCS, CH_3Cl, HCl	0ppm**	0ppm**	0ppm**

*) Aldehydes in CH_3CHO equivalent

**) below detection limit

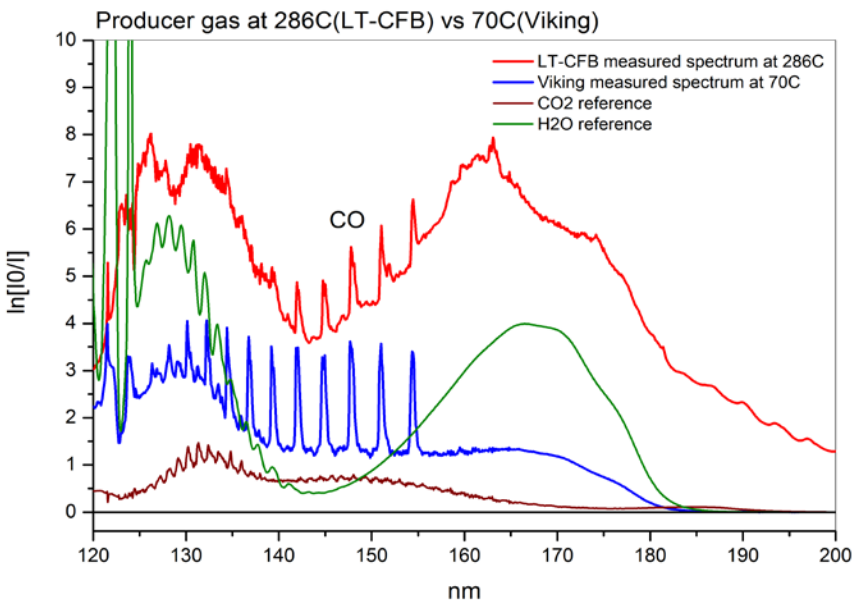
***) concentrations calculated from spectra measured over 10 min measurement time

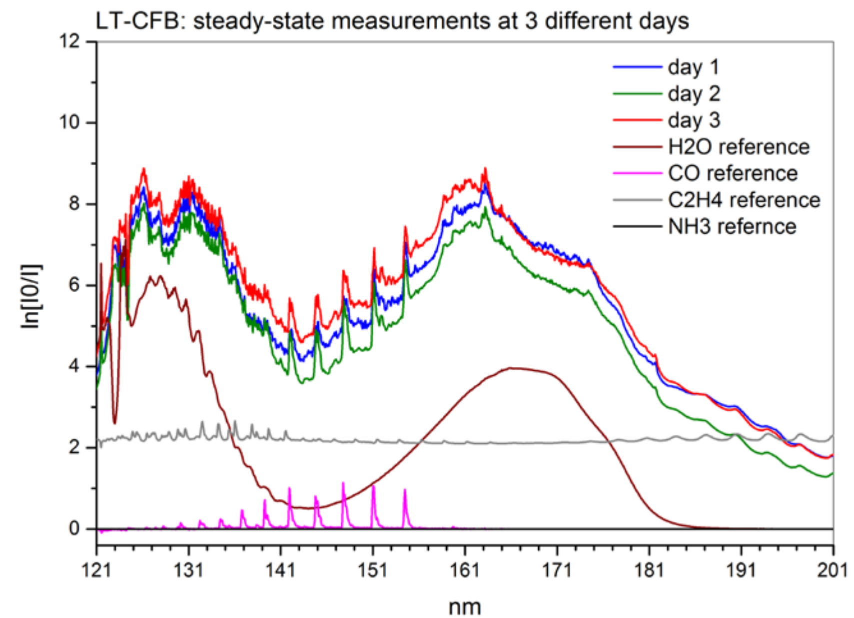
Dirty gas: LT-CFB gasifier: gas extraction at 150C

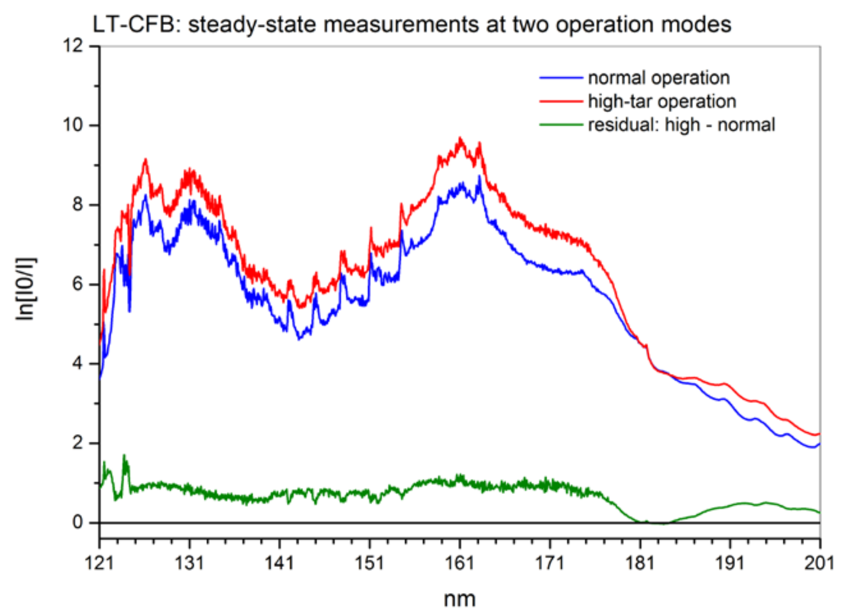


Method	Time	Temperature	Phenol	Naphthalene
GC-MS	30 min	15°C	215 ppm	16 ppm
Extraction	3 min	150°C	360 ppm	31 ppm
In-situ	6 min	400°C	500 ppm	N/A

Dirty gas: LT-CFB gasifier: in situ

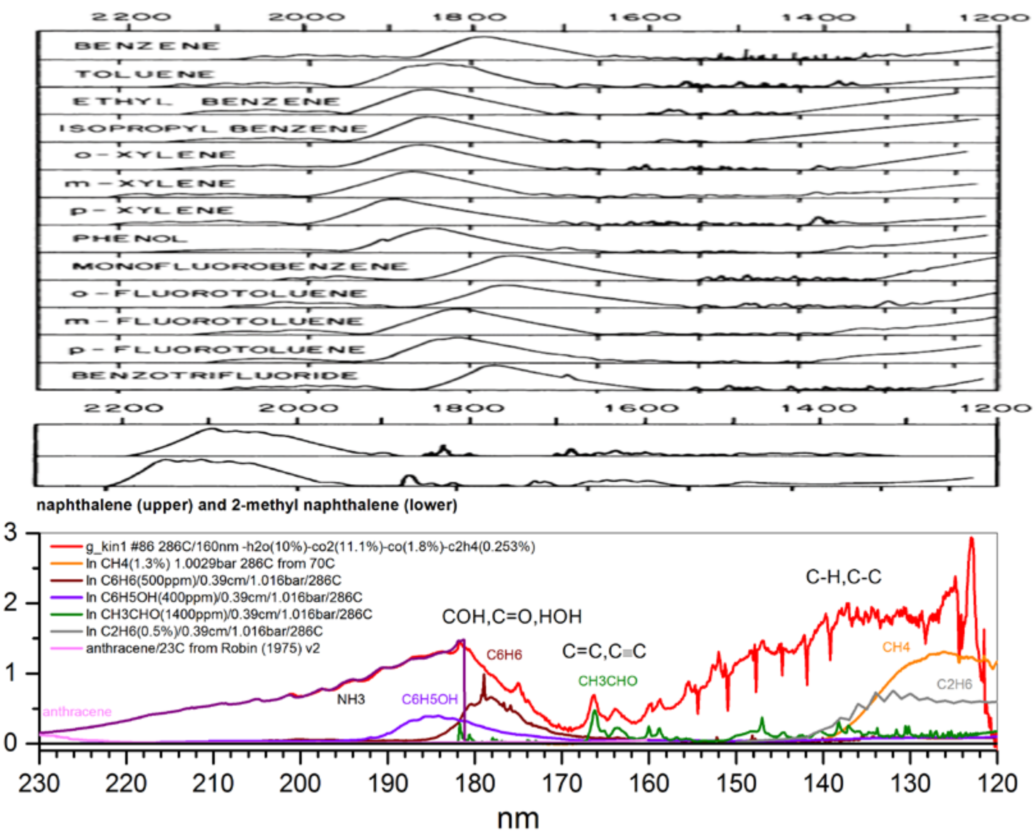






- LT-CFB relatively stable operation in respect to tar/BTX
- “high-tar” operation mode: more BTX/tar (190nm<λ), more NH_3
- In 120-190 nm additional tar absorption gives a base-line like “shift” because nearly flat absorption structures for tar/BTX in 120-170 nm.
- no HCl, CH_3Cl(120ppm)

Dirty gas: LT-CFB gasifier: in situ

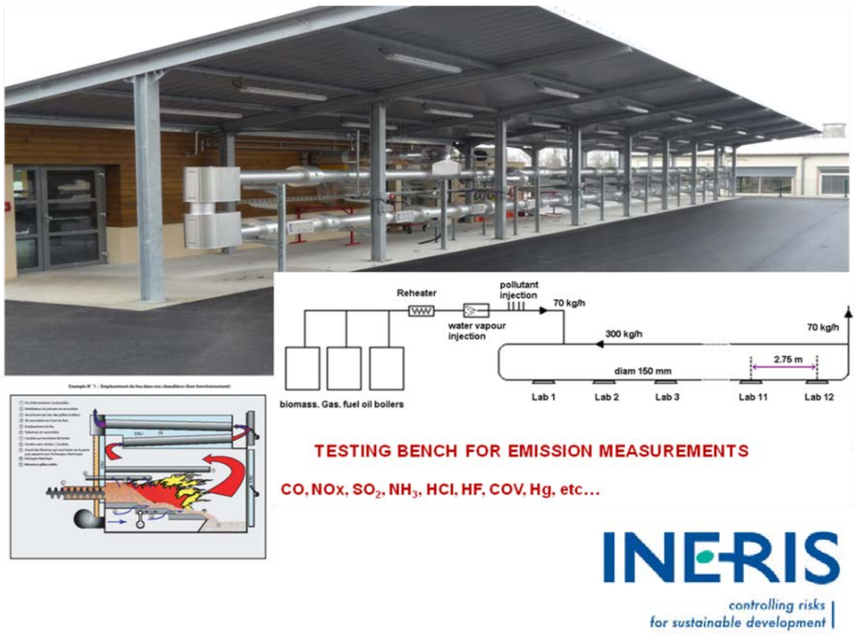


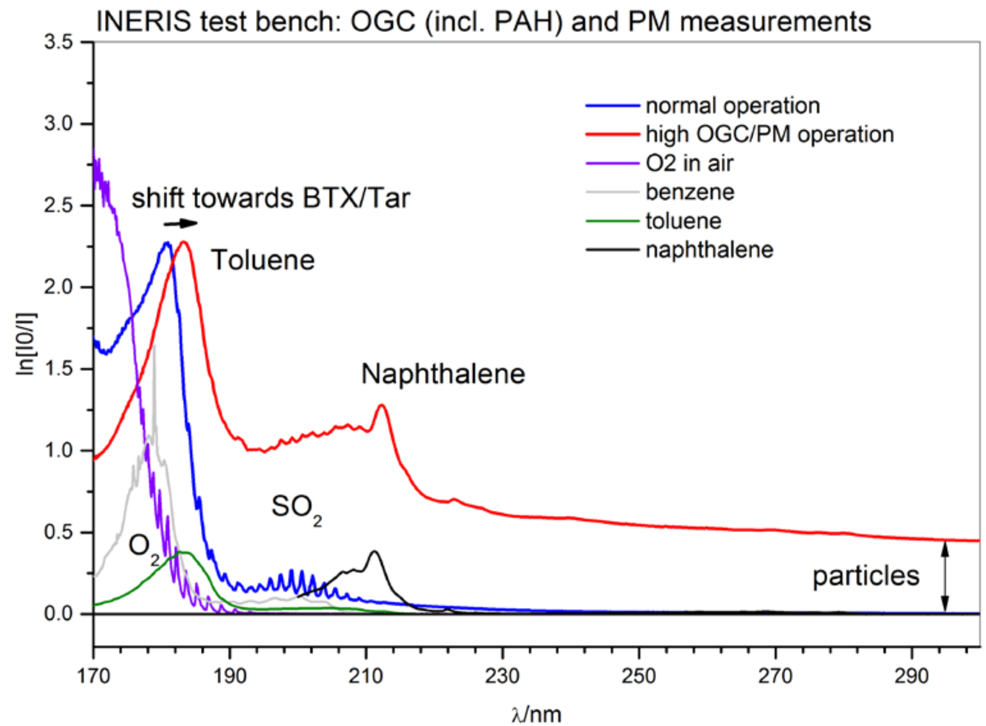
Typical residual spectrum after $H_2O+CO_2+CO+C_2H_4$ subtraction

Tar contribution to the total absorption:

- high: (most absorption (=concentration) due to BTX (170-190nm)
- medium: “light tar” (naphthalene$^+$) (190-220nm)
- low: “heavy tar” (anthracene$^+$) (220nm<λ)

“Bad” grade wood fired burner: incomplete combustion





- “normal” (=optimized) combustion: BTX
- “bad” (=high OGC/PM) combustion: BTX + naphthalene$^+$ + PM
- PM concentration and effective size can be obtained from extinction measurements (absorption + scattering)

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Conclusions

- UV/far UV absorption spectroscopy is a powerful tool for tar and major/minor gas components in situ and on-line measurements
- UV absorption T-dependent cross section databases for various organic molecules are either available or can be generated on request
- Successful demonstration of UV/far UV/DOAS approaches in measurements in various environments (low/high temperature gasification and combustion)
- Tar have about the same absorption cross sections as BTX-family so their contribution into total absorption signal will be proportional to their concentrations
- This can be used for their in situ measurements (absolute or relative) by simple weighting of the 195-230 nm and 170-200 nm areas under an absorption spectrum
- Spectral resolution of the spectrometer does not play any role for this approach and use an ordinary N_2 for purge of the optics would be enough
- Ability unexpansive far UV small spectrometers opens possibility for a new in situ tar/BTX sensor development when a complex tar/BTX sampling can be avoided.

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Thank You

Questions? Comments?